

FORM PTO-1390 (REV. 12-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER <b>722-X02-020</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>10/069209</b>
INTERNATIONAL APPLICATION NO. <b>PCT NO. GB00/03281</b>	INTERNATIONAL FILING DATE <b>AUGUST 24, 2000</b>	PRIORITY DATE CLAIMED <b>AUGUST 24, 1999</b>	
TITLE OF INVENTION <b>GAS SENSOR AND ITS METHOD OF MANUFACTURE</b>			
APPLICANT(S) FOR DO/EO/US <b>MALCOLM TRAYTON AUSTEN; JOHN ROBERT DODGSON</b>			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p style="margin-left: 20px;">a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> is attached hereto.</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p style="margin-left: 20px;">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p style="margin-left: 20px;">b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p style="margin-left: 20px;">c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p style="margin-left: 20px;">d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p><b>Items 11 to 20 below concern document(s) or information included:</b></p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input checked="" type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information:</p> <p style="margin-left: 40px;"><b>COPY OF INT'L PRELIMINARY EXAMINATION REPORT; MARKED-UP SPECIFICATION; 2 SHT DWG; COPY OF PUBLISHED APPLICATION WO 01/14868 A2, CERTIFICATE OF EXPRESS MAILING; POSTCARD</b></p>			

U.S. APPLICATION NO. (if known, see 37 CFR 1.53) <b>107069209</b>		INTERNATIONAL APPLICATION NO. <b>PCT No. GB00/03281</b>		ATTORNEY'S DOCKET NUMBER <b>722-X02-020</b>	
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21. <input checked="" type="checkbox"/> The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. . . . . <b>\$1040.00</b> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO . . . . . <b>\$890.00</b> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO . . . . . <b>\$740.00</b> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . <b>\$710.00</b> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>	
				\$	<b>890.00</b>
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	<b>130.00</b>
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	<b>30</b> - 20 =	<b>10</b>	x <b>\$18.00</b>	\$	<b>180.00</b>
Independent claims	<b>3</b> - 3 =	<b>0</b>	x <b>\$84.00</b>	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+	<b>\$280.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$	<b>1200.00</b>
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+	\$
<b>SUBTOTAL =</b>				\$	
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
<b>TOTAL NATIONAL FEE =</b>				\$	<b>1200.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +				\$	
<b>TOTAL FEES ENCLOSED =</b>				\$	<b>1200.00</b>
				Amount to be refunded:	\$
				charged:	\$

a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. **500601** in the amount of \$ **1200.00** to cover the above fees.  
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
 overpayment to Deposit Account No. **500601**. A duplicate copy of this sheet is enclosed.

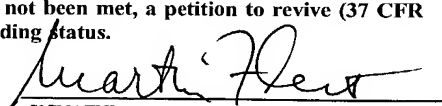
d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO.

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**E-MAIL: MFLEIT@FocusOnIP.COM**

  
 SIGNATURE  
**MARTIN FLEIT**  


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 NAME  
**16,900**  


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 REGISTRATION NUMBER

FORM PTO-1390 (REV. 12-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>722-X02-020</b>	
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**COPY**

PATENT

Attorney Docket No.: 722-X02-020

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicant/Inventor: Malcolm Trayton AUSTEN et al

Serial/Patent No.: National Stage filing of PCT No. GB00/03281      Group Art Unit:

Filed/Issued: February 21, 2002

Examiner:

For/Title: GAS SENSOR AND ITS METHOD OF MANUFACTURE

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D. C. 20231

Dear Sir:

With respect to the above-entitled application, kindly amend as follows:

**IN THE SPECIFICATION**

Please substitute the attached specification (ATTACHMENT I) for the one originally filed. The only change is to add section titles and paragraph numbers.

**IN THE CLAIMS**

Please cancel claim 30 and amend the remaining claims to read as follows; only claims 2 to 17 and 19 to 29 have been amended; a marked-up copy of the claims is attached (ATTACHMENT II).

- - 1. A method of manufacturing a gas sensor having a housing containing a reservoir which in use receives an electrolyte, the method comprising the steps of: impregnating a gas porous membrane with a conductive material, so that said conductive material defines an electrical pathway between an electrical contact on a first surface of the membrane and an electrode on a second surface of the membrane and arranging the membrane to seal the reservoir.

2. A method according to claim 1 further including the step of attaching a wick to the electrode .

3. A method according to claim 2 whereby the wick is pressed or sintered to the electrode .

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4. A method according to claim 3 whereby the wick is sintered to the electrode at a temperature of between 300°C and 370°C.
5. A method according to claim 4 whereby the wick is sintered to the electrode at a temperature of between 320°C and 370°C.
6. A method according to claim 2 whereby the conductive material is introduced into a substrate via the wick.
7. A method according to claim 1 whereby the conductive material is introduced into a substrate via an electrode .
8. A method according to claim 1 whereby the conductive material is introduced into a substrate via an external connection .
9. A method according to claim 1 whereby the conductive material is introduced into a substrate via the substrate .
10. A method according to claim 1 whereby conductive material in its melted state is introduced into a substrate .
11. A method according to claim 1 whereby electrodes and/or external connections are formed on a substrate by one of (a) screen printing, (b) filtering in selected areas from a suspension placed onto the substrate, (c) spray coating, and (d) sintering.
12. A method according to claim 1 whereby electrodes are formed on the opposite faces of a substrate to external connections.
13. A method according to claim 8 whereby the electrodes are formed on the same face of the substrate as the external connections.
14. A method according to claim 1 wherein a substrate and the housing are bonded together using adhesive.
15. A method according claim 1 wherein a substrate and housing are bonded using heat and/or pressure so that material forming the housing melts and impregnates the substrate, thus forming a strong bond therebetween.
16. A method according to claim 1 whereby the permeability of at least one region of a substrate to gas is decreased in order to limit the amount of gas reaching an electrode.

17. A method according to claim 16 whereby the permeability of at least one region of the substrate to gases is decreased by one of a) compressing the region, b) impregnating the regions) with wax, c) impregnating the region(s) with a polymer, and a combination of any of steps a) to c).

18. A gas sensor comprising: at least first and second electrodes formed on a planar substrate; a housing containing a reservoir which, in use, contains liquid electrolyte for contacting the first and second electrodes; an electrical contact for making, external electrical connection from the gas sensor; and a conductive material disposed between an electrode and the external electrical contact, wherein at least a portion of the electrode and a portion of the substrate substantially adjacent thereto, is impregnated with the conductive material, the material forming an electrical pathway through the membrane which connects at least an electrode to the external electrical contact.

19. A gas sensor according to claim 18 wherein the electrodes and/or external connections are formed from a porous electrically conductive material containing catalyst material.

20. A gas sensor according to claim 18 wherein the first electrode is a sensing electrode for creating the desired electrochemical reaction between the electrolyte and the gas to be sensed,

21. A gas sensor according to claim 18 wherein the second electrode is a counter electrode which performs an electrochemical reaction with oxygen.

22. A gas sensor according to claim 18 further including a reference electrode.

23. A gas sensor according to claim 18 further including a gas generating electrode.

24. A gas sensor according to claim 18 wherein a conductive mass includes polymer electrolyte.

25. A gas sensor according to claim 24 wherein the conductive mass is a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes and external connections.

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26. A gas sensor according to claim 18 wherein the external connections includes polymer electrolyte.

27. A gas sensor according to claim 18 wherein external connection is a metal strip, or wire, which is attached to the substrate.

28. A gas sensor according to claim 18 further including a wick, the wick being arranged so that, in use, it contacts both the electrolyte and the electrodes, thereby wetting the electrodes with electrolyte.

29. A gas sensor according to claim 28 wherein the wick has at least one aperture formed therein through which polymer electrolyte can be introduced.

31. A method of forming, an electrical pathway across a microporous membrane having first and second major surfaces; which membrane in use is impervious to liquid and permeable to gas, comprising the steps of: maintaining sufficient heat to melt a conductive material; urging the melted conductive material through pores of the membrane at a first surface by establishing a pressure differential across the surfaces; controlling the heat and pressure differential until the conductive material emerges at the second surface; and allowing the material to cool so as to form a continuous, electrically conductive pathway from the first to the second surface whilst preserving the liquid impermeability and gas permeability characteristics of the membrane. - -

IN THE ABSTRACT

Please cancel the abstract and insert the following new abstract

- - ABSTRACT


The invention relates to an electrochemical gas sensor and its method of manufacture. The gas sensor consists of an external housing, which acts as a reservoir for electrolyte; a wick to keep electrodes wetted with the electrolyte and external electrical terminals, for making electrical contact with the electrodes. The method urges conductive polymer through a membrane under controlled conditions of heat and pressure, thereby ensuring the integrity of the membrane remains intact whilst defining an electrically/conductive pathway therethrough. - -

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### REMARKS

The amendments made above are for the purpose of placing the application in conformity with the formalities required by the Rules of Practice and to enable examination on the merits.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Martin Fleit", with a long horizontal flourish extending to the right.

Martin Fleit, Reg. #16,900

Martin Fleit  
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10/069209

JC19 Rec'd PCT/PTO 22 FEB 2002

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**GAS SENSOR AND ITS METHOD OF MANUFACTURE**

5 The present invention relates to a gas sensor, and to its method of manufacture. It relates particularly, but not exclusively, to an electrochemical gas sensor for sensing carbon monoxide (CO) gas.

An electrochemical gas sensor for sensing an oxidisable or reducible gas, such as carbon monoxide, usually includes a sensing electrode, a counter electrode and a diffusion barrier. The diffusion barrier allows gas to be sensed, to pass to the sensing electrode. In one type of gas sensor, as described, for example, in the Applicant's copending International Patent Application No. WO-A1-9614576, the sensing and counter electrodes are located on a gas permeable membrane and are in  
15 contact with an electrolyte.

In terms of physical construction, electrochemical gas sensors usually comprise an external housing, which acts as a reservoir for electrolyte; a wick, to keep the electrolyte in contact with the electrodes; and external electrical terminals, which  
20 make electrical contact with the electrodes.

During operation of the aforementioned gas sensor, an electrochemical reaction occurs at the sensing electrode with the gas to be sensed, and a reaction also occurs with oxygen at the counter electrode. Electric current is carried through the electrolyte by ions produced in these reactions, and the amount of current indicates  
25 the concentration of the gas being sensed. A further electrode (the reference electrode) may be employed, for example, in combination with a potentiostat circuit, to maintain a constant potential difference between the sensing electrode and the electrolyte. This increases the stability of operation of the gas sensor.

30 Electrodes are connected to external current sensors via electrical terminals.

External electrical terminals are usually formed from brass or copper pins. Brass and copper both react with the acid electrolyte, and so the gas sensor has to be specially designed so that the pins do not come into contact with the electrolyte. Platinum does not react with acid, and so platinum strips can be used to form an electrical path between the electrodes and external sensors and/or an external electricity supply. However, platinum strips are commonly placed in a seal region between the housing and the gas permeable membrane, and electrolyte can leak from this region. Platinum is also expensive, and so gas sensors having platinum terminals are expensive to manufacture.

Another example of a gas sensor is described in US Patent US-A-5314605 (Dragerwerk). The aforementioned US Patent describes a gas permeable region through which holes have been formed. Electrodes pass through the holes. No matter how carefully the region between the periphery of each hole and the electrode is sealed, there is a risk of electrolyte leaking through this seal.

An aim of the present invention is to provide a gas sensor that is cheaper to manufacture than existing gas sensors. Another aim of the invention is to provide a gas sensor that is less prone to leaking than existing gas sensors.

According to a first aspect of the present invention there is provided a method of manufacturing a gas sensor having a housing containing a reservoir which in use receives an electrolyte, the method comprising the steps of: impregnating a gas porous membrane with a conductive material, so that said conductive material defines an electrical pathway between an electrical contact on a first surface of the membrane and an electrode on a second surface of the membrane and arranging the gas porous membrane to seal the reservoir.

Thus in accordance with a first aspect of the invention, a simple and reliable means is provided for connecting one or more electrodes, located within a sealed reservoir of the gas sensor, to an electrical pathway outside the sensor; the method avoiding the use of expensive platinum terminals and one which produces a gas sensor  
5 which is less prone to leaking.

Preferably the conductive material comprises a conductive polymer and is introduced into the pores of a microporous membrane under conditions of heat and pressure.

The method may also include the step of attaching a wicking means to one or more  
10 of the electrodes. The wicking means ensures that each electrode is/are kept in contact with the electrolyte irrespective of the orientation of the sensor once installed. The wicking means may be pressed or sintered to the or each electrode at a temperature of between 300°C and 370°C, most preferably between 320°C and 370°C. The exact temperature depends on the nature of the wicking means, the  
15 electrode material, and the substrate. Attachment of a wicking means may be performed before any melted conductive polymer is introduced, in which case the wicking means may have at least one aperture therein through which melted polymer can pass to an electrode.

According to a second aspect of the invention there is provided a method of  
20 forming an electrical pathway across a microporous membrane having first and second major surfaces; which membrane in use is impervious to liquid and permeable to gas, comprising the steps of: maintaining sufficient heat to melt a conductive material; urging the melted conductive material through pores of the membrane at a first surface by establishing a pressure differential across the  
25 surfaces; controlling the heat and pressure differential until the conductive material emerges at the second surface; and allowing the material to cool so as to form a continuous, electrically conductive pathway from the first to the second surface whilst preserving the liquid impermeability and gas permeability characteristics of the membrane.

Preferably the microporous membrane thereby formed is incorporated into an electrochemical cell which may be incorporated into a gas sensor.

Conductive material may be introduced into the substrate via the wicking means, via the electrodes, via the substrate, or via a combination of these.

- 5 The conductive material preferably includes conductive polymer. On cooling and solidification of the conductive material, an electrical path is formed between the electrode and the electrical contact or external connection means. Electric current generated in use, at the sensing electrode, may thus pass via the microporous membrane, by way of the conductive polymer to the external connection means, and then to a suitable electronic device (or current source in the case of a test gas generator) where the amount of current generated at the sensing electrode can be measured.

- 15 The first and second electrodes are preferably formed from a porous electrically conductive material containing PTFE or similar polymeric binder. Electrodes may also contain particles of catalyst, and optional, additional catalyst support material and material to enhance conductivity.

- 20 Electrodes may be formed on the substrate by, for example, screen printing, filtering in selected areas from a suspension placed onto the substrate, by spray coating, ink jet printing, sintering, or any other method suitable for producing a patterned deposition of solid material. Deposition might be of a single material, or of more than one material sequentially in layers so as, for example, to vary the properties of the electrode material through its thickness.

- 25 Preferably first and second electrodes are formed on an opposite surface of the substrate to the external electrical contact means. Alternatively, the first and second electrodes and the external electrical contact means, may be formed on the same side of the substrate.

The substrate may be bonded to the housing using adhesive. Alternatively, a mechanical means such as a snap-link may be used. It is preferred, however, to

employ heat and/or pressure to bond the substrate to the housing. The housing preferably comprises a synthetic plastics material with a lower melting point than the substrate. When the substrate and the housing are fixed together using heat and/or pressure, housing material impregnates the substrate thereby forming a strong mechanical bond which is also impervious to the electrolyte.

A cap member having a diffusion barrier may also be provided. The substrate is positioned between the cap member and the housing. Heat and/or pressure (or other suitable method) is then applied to seal the sensor assembly. If a cap member is not used, then the permeability of at least one region of the substrate may be modified in order to control the amount of gas reaching the electrodes. This may be achieved by use of a material with the required porosity, or the porosity may be decreased either by i) compressing the region, or ii) by impregnating the region(s) with, for example, wax, polymer, or a wax/polymer mix.

According to a further aspect of the invention there is provided a gas sensor comprising: at least first and second electrodes formed on a planar substrate; a housing containing a reservoir which, in use, contains liquid electrolyte for contacting the first and second electrodes; an electrical contact for making external electrical connection from the gas sensor; and a conductive material disposed between an electrode and the external electrical contact, wherein at least a portion of the electrode and a portion of the substrate substantially adjacent thereto, is impregnated with the conductive material, the material forming an electrical pathway through the membrane which connects at least an electrode to the external electrical contact.

The electrodes are preferably porous planar elements. The first electrode is preferably a gas sensing (working electrode) for creating the desired electrochemical reaction between the electrolyte and the gas to be sensed. The second electrode is preferably a counter electrode which performs the counterpart electrochemical reaction with oxygen. The gas sensor may include further electrodes, such as a reference electrode and/or a test gas generating electrode.

The conductive material may be in the form of a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes and an external connection means.

5 The external electrical contact or connection means is preferably a porous planar element which may be formed on the substrate in an identical manner to the formation of the electrodes. Alternatively, the external connection means may be formed from the same, or a similar material, to the conductive material. The external connection means may also be a metal strip, or wire, which is attached to the substrate.

10 The sensor may have a cap so that the substrate is disposed between the cap and the housing. In this particular arrangement, the substrate is preferably highly gas permeable and presents little or no barrier to diffusion of gas there through. In such an embodiment, diffusion of gas to the sensing electrode is preferably limited by a diffusion barrier located in the cap.

15 Alternatively, the sensor may have no cap, so that the substrate itself acts as a diffusion barrier and forms the upper part of the housing. In this case, porosity of the substrate in certain regions is preferably decreased in order to limit the amount of gas reaching the sensing electrode and/or the counter electrode. The substrate may be flexible, semi-rigid, or rigid.

20 Preferably the electrolyte is sulphuric acid or other suitable electrolyte.

Embodiments of the invention, will now be described, by way of example only, and with reference to the accompanying Figures, in which:-

Figure 1 shows a cross-section of a first gas sensor;

Figure 2 shows a cross-section of a second gas sensor; and

25 Figure 3 shows a sectional view through another gas sensor.

- Referring to Figure 1 there is shown a sectional view of an electrochemical gas sensor 10a in the form of a right circular cylinder, the sensor comprises a two part housing 12a and 12b, a sensing electrode 14, a counter electrode 16, and external contact tracks 28a and 28b formed on a generally circular membrane 18. Electrodes 14 and 16 are formed from a mixture of electrically conductive catalyst particles in PTFE binder, and are screen printed or filter deposited onto the surface of the membrane 18 in the form of segments, as shown in the Figure. External contacts 28a and 28b are formed by urging conductive polymer, which may be loaded with conductive non-catalytic particles, through the membrane 18.
- 10 Housing portion 12b is cylindrical with a hollow interior defining an electrolyte reservoir 20, which in use contains a liquid electrolyte 30. Electrolyte 30 is maintained in contact with the electrodes 14,16 by means of a wick 21. The electrolyte reservoir 20 is closed at the base by means of a base member 32 having a pressure relief vent closed by a porous membrane. Housing part 12a is a disc
- 15 shaped cap member having an aperture 22 therein to permit atmospheric gas to diffuse to a recessed manifold area 24, and then to sensing electrode 14. The housing portions comprise a synthetic plastics material. Aperture 22 may be in the form of a diffusion barrier to control the amount of gas reaching the sensing electrode.
- 20 Membrane 18 is disc shaped and is of approximately the same diameter as lower housing portion 12b. The membrane is disposed between upper housing portion 12a and lower housing portion 12b. As the upper housing portion 12a is smaller in diameter than lower housing portion 12b, external contact tracks 28a and 28b extend beyond the edge of upper housing portion 12a, and may thus be used as an
- 25 external electrical contact or connection. The external electrical contacts may be connected to a printed circuit board and a power supply by way of pins, spring clips, or wires (not shown). A solid polymer 26 is heated and forced under pressure, through the membrane so that it forms contact 28. Details of how this is achieved are described below.

Referring now to Figure 2 which shows a sectional view of the second embodiment 10b of the invention, similar parts to those of Figure 1 are denoted by the same reference numerals. In this embodiment of the invention, the upper cap member 12a is not present. The membrane 18 is of a low permeability to gases in order to define  
5 a diffusion barrier for incoming gas. Thus precise control over the rate of ingress of gas is provided. The permeability of the membrane 18 may be uniform over its entire area, or the permeability may be reduced in a particular region by, for example, pressing or impregnating certain areas of the membrane with a suitable substrate.

10 In gas sensor 10b, regions of the electrodes 14 and 16 and the membrane 18 are impregnated with a conductive polymer 26 such that the conductive polymer 26 protrudes through the membrane 18 to form external contacts 28a and 28b. Further external electrical contact means may then be provided.

One advantage of the gas sensor according to the present invention, over existing  
15 gas sensors is that the electrodes of sensors 10a,b do not extend between the housing and the membrane 18, which are generally the weakest part of the gas sensor assembly. Thus in gas sensors 10a and 10b, a strong seal is formed between the housing and the membrane, and electrolyte is less likely to leak from the sensor.

During operation of gas sensors 10a and 10b, gas from the environment diffuses  
20 through the membrane 18 (via aperture 22 for sensor 10a) to sensing electrode 14. If this gas contains, for example, carbon monoxide, an electrochemical reaction occurs at sensing electrode 14, and an electrochemical reaction with oxygen occurs at counter electrode 16. Current is thus carried through the electrolyte 30 by ions produced in these reactions. The size of the current indicates the concentration of  
25 carbon monoxide.

A reference electrode (not shown) may be employed in combination with a potentiostat circuit (not shown) to maintain the potential between the sensing electrode 14 and the electrolyte 30 in order to increase the stability of the sensor 10a.

The assembly of sensor 10a will now be described. Electrodes 14 and 16 are formed on the lower surface of membrane 18. External contact tracks 28a and 28b are formed on the upper surface of this membrane. The wick 21 is then sintered to the electrodes 14 and 16. Molten conductive polymer 26 is introduced into required areas of the membrane 18 via holes in the wick 21, or from the upper surface of external contract tracks 28a,b, by applying heat and pressure to force the polymer through the membrane so a contact is made between external contacts 28a and 28b and electrodes 14 and 16. On solidification of the polymer 26, an electrical path is formed between the electrolyte 30 contained with electrolyte reservoir 20 and the external contact tracks 28a and 28b.

The membrane is then positioned between upper 12a and lower housing portions 12b, and heat and pressure are applied using a press tool in order to compress the membrane and the external contacts onto the housing portions, thereby bonding the assembly together. Alternatively, one or both of the housing portions 12a,b may be bonded to the membrane 18 using adhesive.

Electrolyte is then introduced into the electrolyte reservoir 20 via aperture 32. This aperture is then plugged with an acid-tight plug (which may be gas permeable), and sealed in place using ultrasonic bonding. This ensures that electrolyte 30 does not leak from the sensor cell 10a.

The assembly of sensor 10b is similar to that of sensor 10a. Electrodes 14 and 16 are formed on the lower surface of the membrane 18. If required, the permeability to gas of regions of the membrane may be decreased, as described previously. The wick 21 is then sintered to the electrodes 14 and 16. Molten conductive polymer 26 is introduced into required areas of the membrane 18 from the upper surface of the membrane 18, by applying heat and pressure to force the material through the membrane so that, on solidification, an amount solidified conductive polymer protrudes through the membrane 18 to form external contacts across porous membrane, without altering its mechanical integrity (i.e. tearing it) but provides an

electrical pathway through membrane 28a and 28b. Further external contact means may be provided, held in place by the solidified conducting polymer.

The membrane is then positioned above lower housing portion 12b, and heat and pressure are applied using a press tool in order to compress the membrane onto the housing portion, thereby bonding the assembly together. Alternatively, the lower housing portion 12b may be bonded to the membrane 18 using adhesive. Electrolyte is then introduced into the electrolyte reservoir 20 as previously described.

Referring to Figure 3, a conductive contact or via 28 is formed by the process of impregnation of the porous membrane or substrate 18 by the conductive material in liquid form. In a preferred method, the substrate 18 is a polymeric material with open porosity, and the material to be impregnated is a polymer with lower melting point than the substrate material, loaded with conductive particles. The impregnating material 26 is forced into the pores of the substrate 18 in liquid form under pressure, so as to form a conductive mass 26 within the pores extending from one side of the substrate to the other. The mean size of the conductive particles may be smaller than that of the pores in the substrate, or may be comparable or larger, in which case the impregnation process and the substrate material are chosen to give sufficient deformation to the pores in the substrate, through heat, pressure or both, to allow the conducting particles to pass through them sufficiently to produce a conductive path.

The conductive material may be introduced by a tool which leaves an amount of the material on the surface on one or both sides which is moulded by the tool (not shown), or in a subsequent process, into a desired shape, for instance to form an electrical contact 28, either to further connection means intended to pass outside the cell or to another similar conductive assembly on a further substrate. The substrate 16 may have an electrode or connector track associated with it, preferably integral

with the substrate and formed on it be for example screen-printing or suction deposition.

In a preferred method, the substrate material is a porous fluoropolymer membrane, for example porous PTFE, and the impregnating material is polypropylene loaded with carbon particles. The melting point of the loaded polypropylene, less than 200°C, is significantly less than that of the PTFE (softening point around 300°C), allowing the polypropylene to be forced through the pores of the PTFE easily by a tool temperature of typically 200-240°C.

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Example: For a PTFE sheet such as **Mupor** (Registered Trade Mark) type 131 (MUPOR Ltd., Alness, UK), thickness 0.2mm with mean pore diameter 2 µm, and impregnating material polypropylene loaded with 40 wt% carbon black particles of mean agglomerate dimension of order 200 nm (material from Whitaker Technical  
15 Plastics Ltd., Macclesfield, UK) good conductivity through the membrane was achieved using a hot pressing technique, at 200-240°C, and a pressure of approximately 200 N/cm<sup>2</sup>, for 10s. This produced a low resistance contact through the membrane to a Pt/PTFE gas diffusion electrode, which was porous with mean pore size similar to that of the membrane, mounted on the opposite side of the  
20 membrane. Such an electrode and contact could be used in a gas sensor as shown in the embodiments described, to detect carbon monoxide.

Figure 3 shows a gas sensor 100 comprises a housing 102 with a reservoir 104 for liquid electrolyte. The reservoir 104 has at its upper end a support member 108 mounted on or attached to the housing to provide a rigid or semi-rigid support for the components connected thereto. The housing 102 has mounted in it contact pins  
25 110, 114, 118 each in good electrical contact with associated moulded components of conducting polymer 112, 116, 120. Overlying the support member 108 is a first electrode assembly consisting of a membrane 122 with a catalyst layer 124. The catalyst material is preferably sintered together with the electrode to produce a  
30 robust electrode assembly. The catalyst layer is formed on the substrate prior to introducing the substrate into the housing, by for example screen-printing, suction

deposition etc. The catalyst layer 124 might be a porous layer formed from a catalytic material such as Pt or RuO<sub>2</sub>, bound together and to the substrate 122 by means of a PTFE binder as is known in the art. Alternatively it might be a nonporous material, for example a metal film, possibly treated to increase its catalytic activity. The substrate 122 is porous and is of a material of higher melting point than the material of the housing 102 and the conducting polymer 120.

The electrode assembly is sealed into the housing with catalyst layer 124 uppermost as shown, by for example application of heat and pressure, or ultrasonic welding. The housing material is locally melted and forced into the porous substrate 122 forming a strong bond in the regions 126. Simultaneously, the conducting polymer, which initially projects above the level of the housing surrounding it, melts and is forced through the substrate 122 and into contact with the electrode 124. If the catalyst is porous then the conducting polymer is preferably forced into the catalyst layer, so improving the electrical contact and physical robustness of the assembly.

A wick assembly 130 overlies the first electrode 124. The wick assembly is compressible and has extensions (shown as dotted outline 132) which reach down into the electrolyte reservoir. A second electrode assembly, consisting of one or more electrodes – two are shown in Figure 3, as 136 and 138 – on a second porous substrate 134, contacts the wick on the opposite side. At least the second electrode 136 consists of a porous catalytic layer capable of reacting signal gas in the presence of air and electrolyte.

The second electrode assembly is sealed to the housing with the catalyst layer lowermost, by application of heat and pressure, ultrasonic welding or similar means as before. The housing material is forced into the substrate 134 forming a bond in the regions 140 and the conducting polymer is melted and impregnated into the electrode 136 and any other electrode that is provided on the common substrate according to details of the embodiment, making electrical contact with them. This second process of sealing and making contact is essentially as described in the

Applicant's granted US patent US 5,914,019. Finally a housing cap 144 is mounted onto the housing 102, by heat sealing, ultrasonic welding or the like. Cap 144 provides access of gas from the exterior to the electrode 136 via the porous substrate 134 and a gas distribution space 148, that access being limited by a diffusion barrier 146, shown in the form of a capillary. The reservoir is partially filled with electrolyte (typically sulphuric acid) via a filling plug in the housing (not shown).

In use, second electrode 136 with gas access from the exterior, acts as the sensing electrode, and first electrode 124 acts as a reference electrode or in a two electrode cell, the counter electrode. If a third electrode 138 is provided, then this acts as the counter electrode.

Variations may be made, for example, the first substrate 122 might have two electrodes on it, with a second conducting polymer and pin contact arrangement to make contact to it, these electrodes functioning as the counter and the reference electrodes, and the second substrate 134 might have just one.

While the contact arrangements 114, 116 and 118, 120 are shown as being at different distances from the edge of the cell, these might be located in any practical geometry as suits the sealing process and tooling, for example, they might be in line with one another relative to the edge. Also, while the sealing surfaces 126 and 140 are shown as being at different levels in the cell, and the seal processes have been described as being done in two stages, especially if very thin components are used these surfaces might be at the same level, with compliance and flexibility of the components optionally being exploited to allow the seals to be made simultaneously.

The contacts are shown as being formed by a contact pin joined to the electrodes by a conductive polymer mass; alternatively, the pin might be absent and the

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conductive polymer might itself lead to the outside of the cell, either with the conductive polymer co-moulded as part of the housing, or it may be bonded to the housing a separate components after moulding.

5 A further variation on this embodiment is in the design of the support means, shown as the support member 108. This could instead comprise a compliant component compressed between the base of the reservoir and the underside of membrane 122, with optional further sheet components to give even support to the components above it.

10

The stacked construction employed in the present invention reduces area used on the common substrate so reducing the "footprint" of the cell; secondly, in planar designs such as that in US 5,914,019 steps must be taken to prevent signal gas from reaching the reference electrode – this implies some form of seal between the edge  
15 of the gas distribution space 148 and the reference electrode. This seal is a source of unreliability and it is a great advantage to avoid need for it. The positioning of the reference electrode on the other side of a wick from the sensing electrode prevents signal gas from reaching it as (i) gas cannot diffuse quickly through the wick and (ii) most if not all signal gas will have reacted at the sensing electrode  
20 anyway.

Variation may be made to the aforementioned embodiments without departing from the scope of the invention. For example, for the sensors described herein, three or more electrodes may be formed on the membrane. These additional electrodes may generate a test gas so that the sensors have self-test capability.

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Claims

1. A method of manufacturing a gas sensor having a housing containing a  
5 reservoir which in use receives an electrolyte, the method comprising the steps  
of: impregnating a gas porous membrane with a conductive material, so that  
said conductive material defines an electrical pathway between an electrical  
contact on a first surface of the membrane and an electrode on a second surface  
of the membrane and arranging the membrane to seal the reservoir.
- 10 2. A method according to claim 1 further including the step of attaching a wicking  
means (21) to the electrodes (14,16).
3. A method according to claim 2 whereby the wicking means (21) is pressed or  
sintered to the electrodes (14,16).
4. A method according to claim 3 whereby the wicking means (21) is sintered to  
15 the electrodes (14,16) at a temperature of between 300°C and 370°C.
5. A method according to claim 4 whereby the wicking means (21) is sintered to  
the electrodes (14,16) at a temperature of between 320°C and 370°C.
6. A method according to any preceding claim whereby the conductive material  
(26) is introduced into the substrate (18) via the wicking means (21).
- 20 7. A method according to any preceding claim whereby the conductive material  
(26) is introduced into the substrate (18) via an electrode (14,16).
8. A method according to any preceding claim whereby the conductive material  
(26) is introduced into the substrate (18) via the external connection means  
(28a,b).

9. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via the substrate (18).
10. A method according to any preceding claim whereby conductive material (26) in its melted state is introduced into the substrate (18).
- 5 11. A method according to any preceding claim whereby electrodes (14,16) and/or external connection means (28a,b) are formed on the substrate (18) by (a) screen printing, (b) filtering in selected areas from a suspension placed onto the substrate, (c) spray coating, or (d) sintering.
12. A method according to any preceding claim whereby the electrodes (14,16) are  
10 formed on the opposite faces of the substrate (18) to the external connection means (28a,b).
13. A method according to any of claims 1 to 8 whereby the electrodes (14,16) are formed on the same face of the substrate (18) as the external connection means (28a,b).
- 15 14. A method according to any preceding claim wherein the substrate (18) and the housing (12a,b) are bonded together using adhesive.
15. A method according to any of claims 1 to 10 wherein the substrate (18) and housing (12a,b) are bonded using heat and/or pressure so that material forming the housing melts and impregnates the substrate, thus forming a strong bond  
20 therebetween.
16. A method according to any preceding claim whereby the permeability of at least one region of the substrate (18) to gas is decreased in order to limit the amount of gas reaching an electrode.
17. A method according to claim 16 whereby the permeability of at least one region  
25 of the substrate (18) to gases is decreased by a) compressing the region, b)

impregnating the region(s) with wax, c) impregnating the region(s) with a polymer, or a combination of any of steps a) to c).

18. A gas sensor comprising: at least first and second electrodes formed on a planar substrate; a housing containing a reservoir which, in use, contains liquid  
5 electrolyte for contacting the first and second electrodes; an electrical contact for making external electrical connection from the gas sensor; and a conductive material disposed between an electrode and the external electrical contact, wherein at least a portion of the electrode and a portion of the substrate substantially adjacent thereto, is impregnated with the conductive material, the  
10 material forming an electrical pathway through the membrane which connects at least an electrode to the external electrical contact.
19. A gas sensor according to claim 18 wherein the electrodes (14,16) and/or external connection means (28a,b) are formed from a porous electrically conductive material containing catalyst material.
- 15 20. A gas sensor according to claims 18 and 19 wherein the first electrode (14) is a sensing electrode for creating the desired electrochemical reaction between the electrolyte (30) and the gas to be sensed.
21. A gas sensor according to any of claims 18 to 20 wherein the second electrode (16) is a counter electrode which performs an electrochemical reaction with  
20 oxygen.
22. A gas sensor according to any of claims 18 to 21 further including a reference electrode.
23. A gas sensor according to any of claims 18 to 22 further including a gas generating electrode.
- 25 24. A gas sensor according to any of claims 18 to 23 wherein the conductive mass (26) includes polymer electrolyte.

25. A gas sensor according to claim 24 wherein the conductive mass (26) is a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes (14,16) and the external connection means (28a,b).
26. A gas sensor according to any of claims 18 to 25 wherein the external  
5 connection means (28a,b) includes polymer electrolyte.
27. A gas sensor according to any of claims 18 to 25 wherein the external connection means (28a,b) is a metal strip, or wire, which is attached to the substrate (18).
28. A gas sensor according to any of claims 18 to 27 further including a wicking  
10 means (21), the wicking means being arranged so that, in use, it contacts both the electrolyte (30) and the electrodes (14,16), thereby wetting the electrodes with electrolyte.
29. A gas sensor according to any of claims 18 to 28 wherein the wicking means (21) has at least one aperture formed therein through which polymer electrolyte  
15 (26) can be introduced.
30. A gas sensor substantially as described herein with reference to the accompanying drawing.
31. A method of forming an electrical pathway across a microporous membrane having first and second major surfaces; which membrane in use is impervious  
20 to liquid and permeable to gas, comprising the steps of: maintaining sufficient heat to melt a conductive material; urging the melted conductive material through pores of the membrane at a first surface by establishing a pressure differential across the surfaces; controlling the heat and pressure differential until the conductive material emerges at the second surface; and allowing the  
25 material to cool so as to form a continuous, electrically conductive pathway from the first to the second surface whilst preserving the liquid impermeability and gas permeability characteristics of the membrane.

**Abstract**

The invention relates to a gas sensor and its method of manufacture.

Electrochemical gas sensors usually comprise an external housing, which acts as a reservoir for electrolyte; a wick to keep electrodes wetted with the electrolyte and  
5 external electrical terminals, for making electrical contact with the electrodes.

Typically a gas permeable/microporous membrane has been used to seal a gas sensor in order to prevent leakage of electrolyte. A problem with existing sensors has been that there was a risk of electrolyte leaking through the membrane around the region where electrical connectors passed therethrough.

10 The present invention overcomes this by providing a method of urging conductive polymer through the membrane under controlled conditions of heat and pressure, thereby ensuring the integrity of the membrane remains in tact whilst defining an electrically/conductive pathway therethrough

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Fig.1.

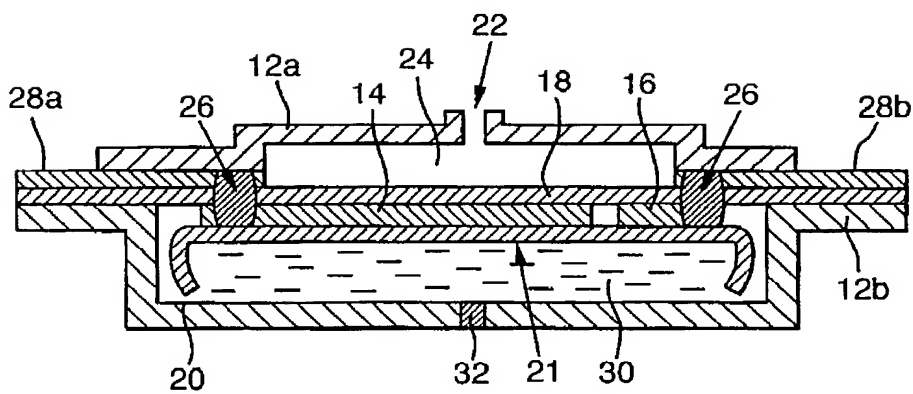
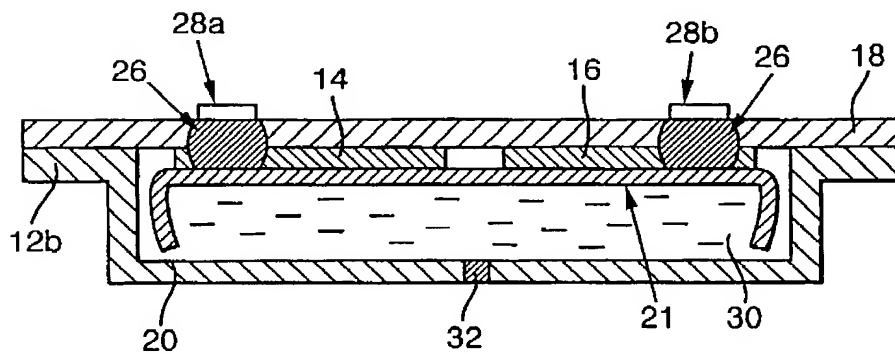
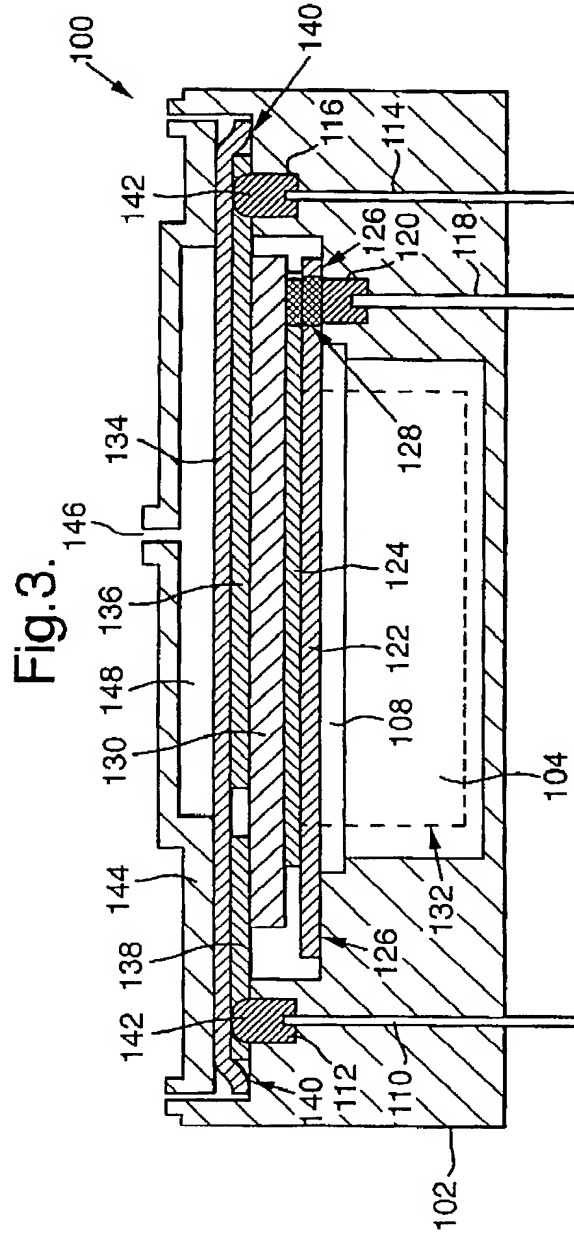


Fig.2.



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## ATTACHMENT II

Marked up copy of amended claims; claims 1, 18 and 31 are unchanged and claim 30 is cancelled.

1. A method of manufacturing a gas sensor having a housing containing a reservoir which in use receives an electrolyte, the method comprising the steps of: impregnating a gas porous membrane with a conductive material, so that said conductive material defines an electrical pathway between an electrical contact on a first surface of the membrane and an electrode on a second surface of the membrane and arranging the membrane to seal the reservoir.

2. A method according to claim 1 further including the step of attaching a wick[ing means (21)] to the electrode[s (14,16)].

3. A method according to claim 2 whereby the wick[ing means (21)] is pressed or sintered to the electrode[s (14,16)].

4. A method according to claim 3 whereby the wick[ing means (21)] is sintered to the electrode[s (14,16)] at a temperature of between 300°C and 370°C.

5. A method according to claim 4 whereby the wick[ing means (21)] is sintered to the electrode[s (14,16)] at a temperature of between 320°C and 370°C.

6. A method according to [any preceding] claim 2 whereby the conductive material [(26)] is introduced into [the] a substrate [(18)] via the wick[ing means (21)].

7. A method according to [any preceding] claim 1 whereby the conductive material [(26)] is introduced into [the] a substrate [(18)] via an electrode [(14,16)].

8. A method according to [any preceding] claim 1 whereby the conductive material [(26)] is introduced into [the] a substrate [(18)] via [the] an external connection [means (28a,b)].

9. A method according to [any preceding] claim 1 whereby the conductive material [(26)] is introduced into[the] a substrate [(18)] via the substrate [(18)].

11. A method according to [any preceding] claim 1 whereby electrodes [(14,16)] and/or external connections [means (28a,b)] are formed on [the] a substrate [(18)] by one of (a) screen printing, (b) filtering in selected areas from a suspension placed onto the substrate, (c) spray coating, [or] and (d) sintering.

13. A method according to [any of claims 1 to] claim 8 whereby the electrodes [(14,16)] are formed on the same face of the substrate [(18)] as the external connections [means (28a,b)].

15. A method according [to any of] claim[s] 1 [to 10] wherein [the] a substrate [(18)] and housing [(12a,b)] are bonded using heat and/or pressure so that material forming the housing melts and impregnates the substrate, thus forming a strong bond therebetween.

17. A method according to claim 16 whereby the permeability of at least one region of the substrate [(18)] to gases is decreased by one of a) compressing the region, b) impregnating the region(s) with wax, c) impregnating the region(s) with a polymer, [or] and a combination of any of steps a) to c).

18. A gas sensor comprising: at least first and second electrodes formed on a planar substrate; a housing containing a reservoir which, in use, contains liquid electrolyte for contacting the first and second electrodes; an electrical contact for making, external electrical connection from the gas sensor; and a conductive material disposed between an electrode and the external electrical contact, wherein at least a portion of the electrode and a portion of the substrate substantially

adjacent thereto, is impregnated with the conductive material, the material forming an electrical pathway through the membrane which connects at least an electrode to the external electrical contact.

19. A gas sensor according to claim 18 wherein the electrodes [(14,16)] and/or external connections [means (28a,b)] are formed from a porous electrically conductive material containing catalyst material.

20. A gas sensor according to claim[s] 18 [and 19] wherein the first electrode [(14)] is a sensing electrode for creating the desired electrochemical reaction between the electrolyte [(30)] and the gas to be sensed,

21. A gas sensor according to [any of] claim[s] 18 [to 20] wherein the second electrode [(16)] is a counter electrode which performs an electrochemical reaction with oxygen.

22. A gas sensor according to [any of] claim[s] 18 [to 21] further including a reference electrode.

23. A gas sensor according to [any of] claim[s] 18 [to 22] further including a gas generating electrode.

24. A gas sensor according to [any of] claim[s] 18 [to 23] wherein [the] a conductive mass [(26)] includes polymer electrolyte.

25. A gas sensor according to claim 24 wherein the conductive mass [(26)] is a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes [(14,16)] and [the] external connections [means (28a,b)].

26. A gas sensor according to [any of] claim[s] 18 [to 25] wherein the external connections [means (28a,b)] includes polymer electrolyte.

27. A gas sensor according to [any of] claim[s] 18 [to 25] wherein [the] external connection [means (28a,b)] is a metal strip, or wire, which is attached to the substrate [(18)].

28. A gas sensor according to [any of] claim[s] 18 [to 27] further including a wick[ing means (21)], the wick[ing means] being arranged so that, in use, it contacts both the electrolyte [(30)] and the electrodes [(14,16)], thereby wetting the electrodes with electrolyte.

29. A gas sensor according to [any of] claim[s 18 to] 28 wherein the wick[ing means (21)] has at least one aperture formed therein through which polymer electrolyte [(26)] can be introduced.

[30. A gas sensor substantially as described herein with reference to the accompanying drawing.]

31. A method of forming, an electrical pathway across a microporous membrane having first and second major surfaces; which membrane in use is impervious to liquid and permeable to gas, comprising the steps of: maintaining sufficient heat to melt a conductive material; urging the melted conductive material through pores of the membrane at a first surface by establishing a pressure differential across the surfaces; controlling the heat and pressure differential until the conductive material emerges at the second surface; and allowing the material to cool so as to form a continuous, electrically conductive pathway from the first to the second surface whilst preserving the liquid impermeability and gas permeability characteristics of the membrane.

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## SUBSTITUTE SPECIFICATION

## **GAS SENSOR AND ITS METHOD OF MANUFACTURE**

### **BACKGROUND OF THE INVENTION**

#### **Field of the Invention**

**[0001]** The present invention relates to a **gas** sensor, and to its method of manufacture. It relates particularly, but not exclusively, to an electrochemical **gas** sensor for sensing carbon monoxide (CO) gas.

#### **Prior Art**

**[0002]** An electrochemical gas sensor for sensing an oxidisable or reducible gas, such as carbon monoxide, usually includes a sensing electrode, a counter electrode and a diffusion barrier. The diffusion barrier allows gas to be sensed, to pass to the sensing electrode. In one type of gas sensor, as described, for example, in the Applicant's copending International Patent Application No. WO-A1-9614576, the sensing and counter electrodes are located on a gas permeable membrane and are in contact with an electrolyte.

**[0003]** In terms of physical construction, electrochemical gas sensors usually comprise an external housing, which acts as a reservoir for electrolyte; a wick, to keep the electrolyte in contact with the electrodes; and external electrical terminals, which make electrical contact with the electrodes.

**[0004]** During operation of the aforementioned gas sensor, an electrochemical reaction occurs at the sensing electrode with the gas to be sensed, and a reaction also occurs with oxygen at the counter electrode. Electric current is carried through the electrolyte by ions produced in these reactions, and the amount of current indicates the concentration of the gas being sensed. A further electrode (the reference electrode) may be

employed, for example, in combination with a potentiostat circuit, to maintain a constant potential difference between the sensing electrode and the electrolyte. This increases the stability of operation of the gas sensor. Electrodes are connected to external current sensors via electrical terminals.

**[0005]** External electrical terminals are usually formed from brass or copper pins. Brass and copper both react with the acid electrolyte, and so the gas sensor has to be specially designed so that the pins do not come into contact with the electrolyte. Platinum does not react with acid, and so platinum strips can be used to form an electrical path between the electrodes and external sensors and/or an external electricity supply. However, platinum strips are commonly placed in a seal region between the housing and the gas permeable membrane, and electrolyte can leak from this region. Platinum is also expensive, and so gas sensors having platinum terminals are expensive to manufacture.

**[0006]** Another example of a gas sensor is described in US Patent US-A-5314605 (Dragerwerk). The aforementioned US Patent describes a gas permeable region through which holes have been formed. Electrodes pass through the holes. No matter how carefully the region between the periphery of each hole and the electrode is sealed, there is a risk of electrolyte leaking through this seal.

## **SUMMARY OF THE INVENTION**

**[0007]** An aim of the present invention is to provide a gas sensor that is cheaper to manufacture than existing gas sensors. Another aim of the invention is to provide a gas sensor that is less prone to leaking than existing gas sensors.

**[0008]** According to a first aspect of the present invention there is provided a method of manufacturing a gas sensor having a housing containing a reservoir which in use receives an electrolyte, the method comprising the steps of: impregnating a gas porous membrane with a conductive material, so that said conductive material defines an electrical pathway between an electrical contact on a first surface of the membrane and an electrode on a second surface of the membrane and arranging the gas porous membrane to seal the reservoir.

**[0009]** Thus in accordance with a first aspect of the invention, a simple and reliable means is provided for connecting one or more electrodes, located within a sealed reservoir of the gas sensor, to an electrical pathway outside the sensor; the method avoiding the use of expensive platinum terminals and one which produces a gas sensor which is less prone to leaking.

**[0010]** Preferably the conductive material comprises a conductive polymer and is introduced into the pores of a microporous membrane under conditions of heat and pressure.

**[0011]** The method may also include the step of attaching a wicking means to one or more of the electrodes. The wicking means ensures that each electrode is/are kept in contact with the electrolyte irrespective of the orientation of the sensor once installed. The wicking means may be pressed or sintered to the or each electrode at a temperature of between 300°C and 370°C, most preferably between 320°C and 370°C. The exact temperature depends on the nature of the wicking means, the electrode material, and the substrate. Attachment of a wicking means may be performed before any melted conductive polymer is introduced, in which case the wicking means may have at least one aperture therein through which melted polymer can pass to an electrode.

**[0012]** According to a second aspect of the invention there is provided a method of forming an electrical pathway across a microporous membrane having first and second major surfaces; which membrane in use is impervious to liquid and permeable to gas, comprising the steps of; maintaining sufficient heat to melt a conductive material; urging the melted conductive material through pores of the membrane at a first surface by establishing a pressure differential across the surfaces; controlling the heat and pressure differential until the conductive material emerges at the second surface; and allowing the material to cool so as to form a continuous, electrically conductive pathway from the first to the second surface whilst preserving the liquid impermeability and gas permeability characteristics of the membrane.

**[0013]** Preferably the microporous membrane thereby formed is incorporated into an electrochemical cell which may be incorporated into a gas sensor.

**[0014]** Conductive material may be introduced into the substrate via the wicking means, via the electrodes, via the substrate, or via a combination of these.

**[0015]** The conductive material preferably includes conductive polymer. On cooling and solidification of the conductive material, an electrical path is formed between the electrode and the electrical contact or external connection means. Electric current generated in use, at the sensing electrode, may thus pass via the microporous membrane, by way of the conductive polymer to the external connection means, and then to a suitable electronic device (or current source in the case of a test gas generator) where the amount of current generated at the sensing electrode can be measured.

**[0016]** The first and second electrodes are preferably formed from a porous electrically conductive material containing PTFE or similar polymeric binder. Electrodes may also contain particles of catalyst, and optional, additional catalyst support material and material to enhance conductivity.

**[0017]** Electrodes may be formed on the substrate by, for example, screen printing, filtering in selected areas from a suspension placed onto the substrate, by spray coating, ink jet printing, sintering, or any other method suitable for producing a patterned deposition of solid material. Deposition might be of a single material, or of more than one material sequentially in layers so as, for example, to vary the properties of the electrode material through its thickness.

**[0018]** Preferably first and second electrodes are formed on an opposite surface of the substrate to the external electrical contact means. Alternatively, the first and second electrodes and the external electrical contact means, may be formed on the same side of the substrate.

**[0019]** The substrate may be bonded to the housing using adhesive. Alternatively, a mechanical means such as a snap-link may be used. It is preferred, however, to employ heat and/or pressure to bond the substrate to the housing. The housing preferably comprises a synthetic plastics material with a lower melting point than the substrate. When the substrate and the housing are fixed together using heat and/or pressure, housing material impregnates the substrate thereby forming a strong mechanical bond which is also impervious to the electrolyte.

**[0020]** A cap member having a diffusion barrier may also be provided. The substrate is positioned between the cap member and the housing. Heat and/or pressure (or other suitable method) is then applied to seal the sensor assembly. If a cap member is not used, then the permeability of at least one

region of the substrate may be to modified in order to control the amount of gas reaching the electrodes, This may be achieved by use of a material with the required porosity, or the porosity may be decreased either by i) compressing the region, or ii) by impregnating the region(s) with, for example, wax, polymer, or a wax/polymer mix.

**[0021]** According to a further aspect of the invention there is provided a gas sensor comprising: at least first and second electrodes formed on a planar substrate; a housing containing a reservoir which, in use, contains liquid electrolyte for contacting the first and second electrodes; an electrical contact for making external electrical connection from the gas sensor; and a conductive material disposed between an electrode and the external electrical contact, wherein at least a portion of the electrode and a portion of the substrate substantially adjacent thereto, is impregnated with the conductive material, the material forming an electrical pathway through the membrane which connects at least an electrode to the external electrical contact.

**[0022]** The electrodes are preferably porous planar elements. The first electrode is preferably a gas sensing (working electrode) for creating the desired electrochemical reaction between the electrolyte and the gas to be sensed. The second electrode is preferably a counter electrode which performs the counterpart electrochemical reaction with oxygen. The gas sensor may include further electrodes, such as a reference electrode and/or a test gas generating electrode.

**[0023]** The conductive material may be in the form of a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes and an external connection means.

**[0024]** The external electrical contact or connection means is preferably a porous planar element which may be formed on the substrate in an identical manner to the formation of the electrodes. Alternatively, the external connection means may be formed from the same, or a similar material, to the conductive material. The external connection means may also be a metal strip, or wire, which is attached to the substrate.

**[0025]** The sensor may have a cap so that the substrate is disposed between the cap and the housing. In this particular arrangement, the substrate is preferably highly gas permeable and presents little or no barrier to diffusion of gas there through. In such an embodiment, diffusion of gas to the sensing electrode is preferably limited by a diffusion barrier located in the cap.

**[0026]** Alternatively, the sensor may have no cap, so that the substrate itself acts as a diffusion barrier and forms the upper part of the housing. In this case, porosity of the substrate in certain regions is preferably decreased in order to limit the amount of gas reaching the sensing electrode and/or the counter electrode. The substrate may be flexible, semi-rigid, or rigid.

**[0027]** Preferably the electrolyte is sulphuric acid or other suitable electrolyte.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

**[0028]** Embodiments of the invention, will now be described, by way of example only, and with reference to the accompanying Figures, in which:

**[0029]** Figure 1 shows a crass-section of a first gas sensor;

**[0030]** Figure 2 shows a cross-section of a second gas sensor; and

**[0031]** Figure 3 shows a sectional view through another gas sensor.

## **DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION**

**[0032]** Referring to Figure 1 there is shown a sectional view of an electrochemical gas sensor 10a in the form of a right circular cylinder, the sensor comprises a two part housing 12a and 12b, a sensing electrode 14, a counter electrode 16, and external contact tracks 28a and 28b formed on a generally circular membrane 18. Electrodes 14 and 16 are formed from a mixture of electrically conductive catalyst particles in PTFE binder, and are screen printed or filter deposited onto the surface of the membrane 18 in the form of segments, as shown in the Figure. External contacts 28a and 28b are formed by urging conductive polymer, which may be loaded with conductive non-catalytic particles, through the membrane 18.

**[0033]** Housing portion 12b is cylindrical with a hollow interior defining an electrolyte reservoir 20, which in use contains a liquid electrolyte 30. Electrolyte 30 is maintained in contact with the electrodes 14,16 by means of a wick 21. The electrolyte reservoir 20 is closed at the base by means of a base member 32 having a pressure relief vent closed by a porous membrane. Housing part 12a is a disc shaped cap member having an aperture 22 therein to permit atmospheric gas to diffuse to a recessed manifold area 24, and then to sensing electrode 14. The housing portions comprise a synthetic plastics material. Aperture 22 may be in the form of a diffusion barrier to control the amount of gas reaching the sensing electrode.

**[0034]** Membrane 18 is disc shaped and is of approximately the same diameter as lower housing portion 12b. The membrane is disposed between upper housing portion 12a and lower housing portion 12b. As the upper

housing portion 12a is smaller in diameter than lower housing portion 12b, external contact tracks 28a and 28b extend beyond the edge of upper housing portion 12a, and may thus be used as an external electrical contact or connection. The external electrical contacts may be connected to a printed circuit board and a power supply by way of pins, spring clips, or wires (not shown). A solid polymer 26 is heated and forced under pressure, through the membrane so that it forms contact 28. Details of how this is achieved are described below.

**[0035]** Referring now to Figure 2 which shows a sectional view of the second embodiment 10b of the invention, similar parts to those of Figure 1 are denoted by the same reference numerals. In this embodiment of the invention, the upper cap member 12a is not present. The membrane 18 is of a low permeability to gases in order to define a diffusion barrier for incoming gas. Thus precise control over the rate of ingress of gas is provided. The permeability of the membrane 18 may be uniform over its entire area, or the permeability may be reduced in a particular region by, for example, pressing or impregnating certain areas of the membrane with a suitable substrate.

**[0036]** In gas sensor 10b, regions of the electrodes 14 and 16 and the membrane 18 are impregnated with a conductive polymer 26 such that the conductive polymer 26 protrudes through the membrane 18 to form external contacts 28a and 28b. Further external electrical contact means may then be provided.

**[0037]** One advantage of the gas sensor according to the present invention, over existing gas sensors is that the electrodes of sensors 10a,b do not extend between the housing and the membrane 18, which are generally the weakest part of the gas sensor assembly. Thus in gas sensors

10a and 10b, a strong seal is formed between the housing and the membrane, and electrolyte is less likely to leak from the sensor.

**[0038]** During operation of gas sensors 10a and 10b, gas from the environment diffuses 20 through the membrane 18 (via aperture 22 for sensor 10a) to sensing electrode 14. If this gas contains, for example, carbon monoxide, an electrochemical reaction occurs at sensing electrode 14, and an electrochemical reaction with oxygen occurs at counter electrode 16. Current is thus carried through the electrolyte 30 by ions produced in these reactions. The size of the current indicates the concentration of carbon monoxide.

**[0039]** A reference electrode (not shown) may be employed in combination with a potentiostat circuit (not shown) to maintain the potential between the sensing electrode 14 and the electrolyte 30 in order to increase the stability of the sensor 10a.

**[0040]** The assembly of sensor 10a will now be described. Electrodes 14 and 16 are formed on the lower surface of membrane 18. External contact tracks 28a and 28b are formed on the upper surface of this membrane. The wick 21 is then sintered to the electrodes 14 and 16. Molten conductive polymer 26 is introduced into required areas of the membrane 18 via holes in the wick 21, or from the upper surface of external contract tracks 28a,b, by applying heat and pressure to force the polymer through the membrane so a contact is made between external contacts 28a and 28b and electrodes 14 and 16. On solidification of the polymer 26, an electrical path is formed between the electrolyte 30 contained with electrolyte reservoir 20 and the external contact tracks 28a and 28b.

**[0041]** The membrane is then positioned between upper 12a and lower housing portions 12b, and heat and pressure are applied using a press tool in

order to compress the membrane and the external contacts onto the housing portions, thereby bonding the assembly together. Alternatively, one or both of the housing portions 12a,b may be bonded to the membrane 18 using adhesive.

**[0042]** Electrolyte is then introduced into the electrolyte reservoir 20 via aperture 32. This aperture is then plugged with an acid-tight plug (which may be gas permeable), and sealed in place using ultrasonic bonding. This ensures that electrolyte 30 does not leak from the sensor cell 10a.

**[0043]** The assembly of sensor 10b is similar to that of sensor 10a. Electrodes 14 and 16 are formed on the lower surface of the membrane 18. If required, the permeability to gas of regions of the membrane may be decreased, as described previously. The wick 21 is then sintered to the electrodes 14 and 16. Molten conductive polymer 26 is introduced into required areas of the membrane 18 from the upper surface of the membrane 18, by applying heat and pressure to force the material through the membrane so that, on solidification, an amount solidified conductive polymer protrudes through the membrane 18 to form external contacts across porous membrane, without altering its mechanical integrity (i.e. tearing it) but provides an electrical pathway through membrane 28a and 28b. Further external contact means may be provided, held in place by the solidified conducting polymer.

**[0044]** The membrane is then positioned above lower housing portion 12b, and heat and pressure are applied using a press tool in order to compress the membrane onto the housing portion, thereby bonding the assembly together. Alternatively, the lower housing portion 12b may be bonded to the membrane 18 using adhesive. Electrolyte is then introduced into the electrolyte reservoir 20 as previously described.

**[0045]** Referring to Figure 3, a conductive contact or via 28 is formed by the process of impregnation of the porous membrane or substrate 18 by the conductive material in liquid form. In a preferred method, the substrate 18 is a polymeric material with open porosity, and the material to be impregnated is a polymer with lower melting point than the substrate material, loaded with conductive particles. The impregnating material 26 is forced into the pores of the substrate 18 in liquid form under pressure, so as to form a conductive mass 26 within the pores extending from one side of the substrate to the other. The mean size of the conductive particles may be smaller than that of the pores in the substrate, or may be comparable or larger, in which case the impregnation process and the substrate material are chosen to give sufficient deformation to the pores in the substrate, through heat, pressure or both, to allow the conducting particles to pass through them sufficiently to produce a conductive path.

**[0046]** The conductive material may be introduced by a tool which leaves an amount of the material on the surface on one or both sides which is moulded by the tool (not shown), or in a subsequent process, into a desired shape, for instance to form an electrical contact 28, either to further connection means intended to pass outside the cell or to another similar conductive assembly on a further substrate. The substrate 16 may have an electrode or connector track associated with it, preferably integral with the substrate and formed on it by for example screen-printing or suction deposition.

**[0047]** In a preferred method, the substrate material is a porous fluoropolymer membrane, for example porous PTFE, and the impregnating material is polypropylene loaded with carbon particles. The melting point of the loaded polypropylene, less than 200°C, is significantly less than that of the PTFE (softening point around 300°C), allowing the polypropylene to be

forced through the pores of the PTFE easily by a tool temperature of typically 200-240°C.

**[0048]** Example: For a PTFE sheet such as Mupor (Registered Trade Mark) type 131 (MUPOR Ltd., Alness, UK), thickness 0.2mm with mean pore diameter 2  $\mu\text{m}$ , and impregnating material polypropylene loaded with 40 wt % carbon black particles of mean agglomerate dimension of order 200 nm (material from Whitaker Technical Plastics Ltd., Macclesfield, UK) good conductivity through the membrane was achieved using a hot pressing technique, at 200-240°C, and a pressure of approximately 200 N/cm<sup>2</sup>, for 10s. This produced a low resistance contact through the membrane to a Pt/PTFE gas diffusion electrode, which was porous with mean pore size similar to that of the membrane, mounted on the opposite side of the membrane. Such an electrode and contact could be used in a gas sensor as shown in the embodiments described, to detect carbon monoxide.

**[0049]** Figure 3 shows a gas sensor 100 comprises a housing 102 with a reservoir 104 for liquid electrolyte. The reservoir 104 has at its upper end a support member 108 mounted on or attached to the housing to provide a rigid or semi-rigid support for the components connected thereto. The housing 102 has mounted in it contact pins 110, 114, 118 each in good electrical contact with associated moulded components of conducting polymer 112, 116, 120. Overlying the support member 108 is a first electrode assembly consisting of a membrane 122 with a catalyst layer 124. The catalyst material is preferably sintered together with the electrode to produce a robust electrode assembly. The catalyst layer is formed on the substrate prior to introducing the substrate into the housing, by for example screen-printing, suction deposition etc. The catalyst layer 124 might be a porous layer formed from a catalytic material such as Pt or RuO<sub>2</sub>, bound together and to the substrate 122 by means of a PTFE binder as is known in the art. Alternatively it might be a nonporous material, for example a metal film,

possibly treated to increase its catalytic activity. The substrate 122 is porous and is of a material of higher melting point than the material of the housing 102 and the conducting polymer 120.

**[0050]** The electrode assembly is sealed into the housing with catalyst layer 124 uppermost as shown, by for example application of heat and pressure, or ultrasonic welding. The housing material is locally melted and forced into the porous substrate 122 forming a strong bond in the regions 126. Simultaneously, the conducting polymer, which initially projects above the level of the housing surrounding it, melts and is forced through the substrate 122 and into contact with the electrode 124. If the catalyst is porous then the conducting polymer is preferably forced into the catalyst layer, so improving the electrical contact and physical robustness of the assembly.

**[0051]** A wick assembly 130 overlies the first electrode 124. The wick assembly is compressible and has extensions (shown as dotted outline 132) which reach down into the electrolyte reservoir. A second electrode assembly, consisting of one or more electrodes - two are shown in Figure 3, as 136 and 138 - on a second porous substrate 134, contacts the wick on the opposite side. At least the second electrode 136 consists of a porous catalytic layer capable of reacting signal gas in the presence of air and electrolyte.

**[0052]** The second electrode assembly is sealed to the housing with the catalyst layer lowermost, by application of heat and pressure, ultrasonic welding or similar means as before. The housing material is forced into the substrate 134 forming a bond in the regions 140 and the conducting polymer is melted and impregnated into the electrode 136 and any other electrode that is provided on the common substrate 30 according to details of the embodiment, making electrical contact with them. This second process of

sealing and making contact is essentially as described in the Applicant's granted US patent US 5,914,019. Finally a housing cap 144 is mounted onto the housing 102, by heat sealing, ultrasonic welding or the like. Cap 144 provides access of gas from the exterior to the electrode 136 via the porous substrate 134 and a gas distribution space 148, that access being limited by a diffusion barrier 146, shown in the form of a capillary. The reservoir is partially filled with electrolyte (typically sulphuric acid) via a filling plug in the housing (not shown).

**[0053]** In use, second electrode 136 with gas access from the exterior, acts as the sensing electrode, and first electrode 124 acts as a reference electrode or in a two electrode cell, the counter electrode. If a third electrode 138 is provided, then this acts as the counter electrode.

**[0054]** Variations may be made, for example, the first substrate 122 might have two electrodes on it, with a second conducting polymer and pin contact arrangement to make contact to it, these electrodes functioning as the counter and the reference electrodes, and the second substrate 134 might have just one.

**[0055]** While the contact arrangements 114, 116 and 118, 120 are shown as being at different distances from the edge of the cell, these might be located in any practical geometry as suits the sealing process and tooling, for example, they might be in line with one another relative to the edge. Also, while the sealing surfaces 126 and 140 are shown as being at different levels in the cell, and the seal processes have been described as being done in two stages, especially if very thin components are used these surfaces might be at the same level, with compliance and flexibility of the components optionally being exploited to allow the seals to be made simultaneously,

**[0056]** The contacts are shown as being formed by a contact pin joined to the electrodes by a conductive polymer mass; alternatively, the pin might be absent and the conductive polymer might itself lead to the outside of the cell, either with the conductive polymer co-moulded as part of the housing, or it may be bonded to the housing a separate components after moulding.

**[0057]** A further variation on this embodiment is in the design of the support means, shown as the support member 108. This could instead comprise a compliant component compressed between the base of the reservoir and the underside of membrane 122, with optional further sheet components to give even support to the components above it.

**[0058]** The stacked construction employed in the present invention reduces area used on the common substrate so reducing the "footprint" of the cell; secondly, in planar designs such as that in US 5,914,019 steps must be taken to prevent signal gas from reaching the reference electrode - this implies some form of seal between the edge of the gas distribution space 148 and the reference electrode. This seal is a source of unreliability and it is a great advantage to avoid need for it. The positioning of the reference electrode on the other side of a wick from the sensing electrode

**[0059]** prevents signal gas from reaching it as (i) gas cannot diffuse quickly through the wick and (ii) most if not all signal gas will have reacted at the sensing electrode anyway.

**[0060]** Variation may be made to the aforementioned embodiments without departing from the scope of the invention. For example, for the sensors described herein, three or more electrodes may be formed on the membrane. These additional electrodes may generate a test gas so that the sensors have self-test capability.

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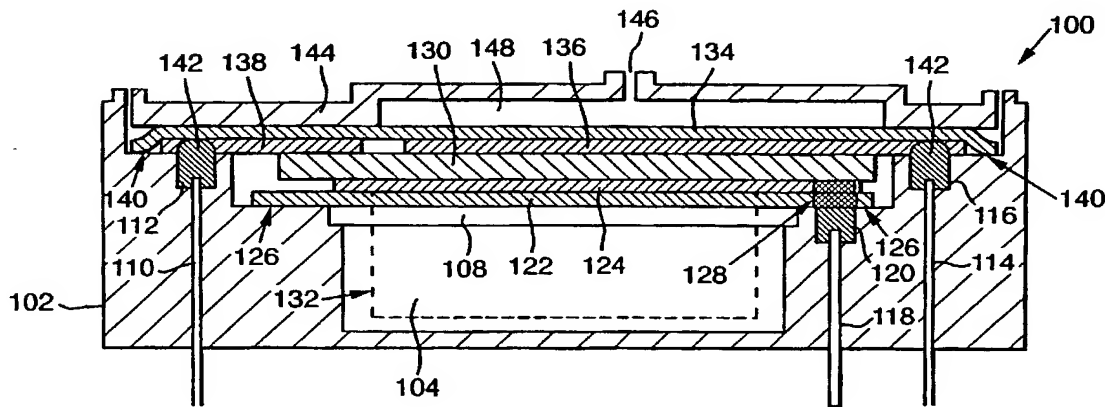
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(57) Abstract: The invention relates to a gas sensor and its method of manufacture. Electrochemical gas sensors usually comprise an external housing, which acts as a reservoir for electrolyte; a wick to keep electrodes wetted with the electrolyte and external electrical terminals, for making electrical contact with the electrodes. Typically a gas permeable/microporous membrane has been used to seal a gas sensor in order to prevent leakage of electrolyte. A problem with existing sensors has been that there was a risk of electrolyte leaking through the membrane around the region where electrical connector passed therethrough. The present invention overcomes this by providing a method of urging conductive polymer through the membrane under controlled conditions of heat and pressure, thereby ensuring the integrity of the membrane remains intact whilst defining an electrically/conductive pathway therethrough.

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**DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter that is claimed and for which a patent is sought on the invention entitled

**GAS SENSOR AND ITS METHOD OF MANUFACTURE**

the specification of which:

  X   was filed  
under Attorney's Docket Number 722-X02-020  
as U.S. Patent Application No. 10/069,209 with the USPTO on Feb. 22, 2002.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information material to the patentability of this application in accordance with 37 CFR 1.56.

I hereby claim the benefit of foreign priority under 35 USC 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate or of any PCT international application having a filing date before that of the application the priority of which is claimed:

Prior Foreign Application(s):			Priority Claimed
Number	Country	Filing Date	Yes No
9919906.9	United Kingdom	Aug. 24, 1999	XXX

I hereby claim the benefit of United States priority under 35 USC 120 of any United States application(s) or 365(c) of any PCT international applications designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is disclosed in a listed one of the prior United States or PCT international application in the manner provided by the first paragraph of 35 USC 112, I acknowledge the duty to disclose information material to the patentability of this

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POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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